

ISSN 2181-8622

Manufacturing technology problems



Scientific and Technical Journal Namangan Institute of Engineering and Technology

INDEX  COPERNICUS
INTERNATIONAL

**Volume 10
Issue 4
2025**



NamMTI ILMIY-TEXNIKA JURNALI TAHRIR HAY'ATI A'ZOLARI

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UDC 661.635.448.547.992.2

METHOD FOR PRODUCING BIOSUPERPHOSPHATE FERTILIZERS CONTAINING HUMIC COMPOUNDS

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Abstract: The purpose of the research is to develop effective technologies for the production of complex mineral fertilizers enriched with calcium, sulfur, phosphorus, nitrogen, sulfur, and humic compounds. To conduct the experiments, ground phosphate raw materials, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sulfur, urea, and leonardite (total humus content 52.3-64.5%; organic matter 66.7-71.1%; moisture content 26.53-33.07%) were used as starting materials. The research was conducted in a glass reactor equipped with a vane stirrer and placed in a thermostated container. In a thermostated beaker, ground phosphate raw materials, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sulfur, urea, and leonardite (total humus content 52.3-64.5%) were placed and mixed with water, then the resulting suspension was intensively stirred for 10 minutes at 70-80°C.

Keywords: Uzbekistan, Central Kyzylkum phosphorites, phosphate raw materials, phosphogypsum, humic substances (HS), ammonium phosphate (ammonium phosphate), simple superphosphate, natural gypsum, urea, humic acids, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur.

Introduction. The global agrochemical complex is a key component of economic development, and the well-being of the population depends on its development. In this regard, it is necessary to provide the agro-industrial complex with a wide range of plant protection products, plant growth and development stimulants, and mineral fertilizers containing basic macroelements in various proportions, including nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. According to the OOH, it is known that the number of people on Earth has increased from 3.7 billion in 1970 to 7.8 billion in 2020 and will exceed 15 billion by 2075. The largest growth will be in Asia. Due to population growth, the problem of food security and the development of industrial agricultural crops is particularly acute. Solving such problems is impossible without expanding the raw material base for the production of high-quality mineral fertilizers and intensifying their technology. At the same time, it is important not only to increase the norms of mineral fertilizers, but also to expand their range to increase crop yields. In this direction, the development and implementation of technology for obtaining calcium and sulfur-containing nitrogen-phosphorus fertilizers is of great importance. In Uzbekistan,

concentrated phosphorus fertilizers currently primarily use ammophos derived from the phosphorites of the Central Kyzylkum. As a result of the application of ammophos, the amount of soluble and plant-absorbed calcium, magnesium, and sulfur compounds introduced into the soil decreases annually, which, in turn, leads to a deficiency of these elements in the body of animals and plants[1].

In this process, the soil loses so much calcium that it is no longer sufficient for the complete neutralization of humic and other acids. As a result, an acidic environment is created, humus is destroyed and washed out, and soil salinization begins. Calcium-demanding plants cannot exist here, they are replaced by typical "sour" taiga plants. For many regions of humid climate, calcium deficiency is characteristic, where domestic animals are small in stature, their skeleton is weak, cow milk yield decreases, they get rickets, eggshells are thinner, etc., since calcium phosphates are the main components in the formation of the skeleton of living organisms. If these compounds are insufficient, even ugliness of offspring is expected. Calcium-rich soils have a neutral or slightly alkaline reaction, are not podzolized, and are very fertile. Calcium neutralizes acidity and stabilizes the organic matter of soil humus - the decomposition products of plant residues. Some scientists suggest returning to the technology of producing simple superphosphate. However, simple superphosphate contains only 14-16% P₂O₅ and a significant amount of calcium sulfate. Firstly, this leads to high costs for transportation, loading and unloading operations, storage, and application of fertilizers. Secondly, geobiochemical processes differ sharply from chemical processes occurring in a flask without the participation of microorganisms. For example, calcium sulfate salts the soil and, with the help of microorganisms, interacts with organic matter (in the absence of oxygen in swampy soil), forming hydrogen sulfide:



In this process, microorganisms oxidize sugar to CO₂ and H₂O due to the oxygen they extract from sulfates. They use the energy released during this process for life activity. In the presence of oxygen, other groups of bacteria can oxidize hydrogen sulfide to elemental sulfur and sulfuric acid[2].

Currently, worldwide, along with mineral fertilizers, increasing attention is being paid to the application and production of humic fertilizers, expanding their raw material base, analysis methods, application methods, and production technologies. Integrated systems for applying mineral fertilizers in combination with organic fertilizers are being developed to create the most optimal conditions for plant development and obtain high and quality yields, taking into account soil conditions, plant species, and other conditions. The use of mineral fertilizers with organic fertilizers in a balanced form has a positive effect on soil fertility, yield, and its quality, and does not lead to environmental pollution[3].

The positive effect of humic substances on soil properties and plant life was noted as early as the end of the 19th century. Humic substances (HM) are naturally occurring high-molecular-weight polymers of irregular structure, formed in the biosphere (soil,

peat, coal, natural waters) as a result of transformations of dead biomass. Currently, their biospheric functions have been identified and formulated. The prospects of using them as soil conditioners to improve soil properties or remedies for polluted natural environments have been shown. Thanks to this, the production of a wide range of industrial humic preparations (IP) from various sources - coal, peat, sapropels, organic waste - has been mastered. GPs are used as organic fertilizers, plant growth stimulants, restorers of disturbed soils, and sorbents of toxic pollutants. The possibility of using humic compounds for the detoxification of pollutants of both organic (oil products) and inorganic (heavy metals) nature is known.

Due to their two-membered chemical structure (the presence of a well-hydrolyzable peripheral part and a non-hydrolyzable nucleus), as well as a wide variety of functional groups, hydrophilic and hydrophobic groups, humic substances are of great interest as detoxifying agents. However, their mechanism of action has not been sufficiently studied. The main raw materials for GP production are peat and some grades of brown coal (mainly Leonardite). The advantage of this raw material is its availability in various regions of the world. In addition, other types of organic raw materials are used - sapropel, vermicompost, organic waste[4].

Due to the peculiarities of their composition and structure, polyfunctionality, humic substances participate in various reactions. The high chemical activity of humic substances allows for the modification of their composition and the synthesis of products with specified properties. It has been established that mechanochemical modification increases the surface activity of humic acids[5].

Soil is a highly complex ecosystem critical to the functioning of the biosphere, and diagnostics is a key aspect of environmental monitoring. Soil performs many irreplaceable functions: regulates water balance, provides plants with nutrients, filters pollutants, serves as a habitat for a huge number of living organisms from microscopic bacteria and fungi to large invertebrates and even some vertebrates. One of the most important components of soil, determining its properties and functions, is organic carbon. Humic acids (HAs) are a raw material for obtaining highly effective humic preparations (HPs) - prolonged-release plant growth stimulants. GC fragments with greater lability can reach the surface of roots and interact with the cell membrane, regulating cellular metabolism. Humic acids contain aromatic and aliphatic domains, representing O-, N-, and S-containing functional groups with high biological and chemical activity, which can influence enzyme activity, stimulate root growth, and increase biomass.

Methods. World agricultural experience has shown that the rational use of natural and soil resources, the development of effective technologies, and the creation of fertilizers with an increased efficiency coefficient on their basis necessitate the solution of a number of scientific and practical problems ensuring the ecological balance of soils. Therefore, the development of new rational technologies for processing organic resources of plant origin, phosphate raw materials, phosphogypsum, and agro-ores into fertilizers containing all the nutrients necessary for the normal growth and development of plants

and ensuring the preservation of soil fertility is a criterion for increasing agricultural productivity [6,7].

The work presents the main principles of composting, according to which the main scientific principle of composting consists of the processes of obtaining phosphorus-humus fertilizers by composting cattle manure (Cattle manure) with Central Kyzylkum sludge phosphorite (SF) with the addition of phosphogypsum (PG) at a mass ratio of Manure: SF: PG= 100: 10: (2-20). It has been shown that in the studied ratios, the greater the mass fraction of FG in the mixture and the longer the composting time, the higher the degree of conversion of the organic part of the manure into humus substances and the transition of the undigestible form of phosphorus from the phosphate raw material into the form assimilable by plants. It has been shown that with an increase in the phosphogypsum content in the compost from 2 to 20%, nitrogen loss decreases from 14.68% to 9.89%, and organic matter losses from 18.65% to 11.08%[8].

Humic acids are polydisperse systems, and to separate them into fractions using solvents, not only ethyl alcohol is widely used, the use of which is associated with the partial esterification of humic acids, but also acetone, furfural, phenol, tetrahydrofuran, etc. The fractions that dissolve in these solvents are often called hematomelanoic acids. However, at present, it is inappropriate to use this obsolete term, introduced about a century ago for the alcohol-soluble fraction of peat humic acids.

The mechanism of isolation of humic and hymatomelanic acids is not yet fully understood. There is reason to believe that these processes are somewhat more complex than the separation of a mechanical mixture of acids. Hymatomelanic acids are found mainly in the fraction of humic acids that is separated from oxidized coals by aqueous alkali without preliminary treatment with hydrochloric acid. Using the example of the formation of hematomelanoic acids, the idea of a sequential-parallel course of the oxidation reaction of coals during the weathering process has been confirmed. Humic acids are prone to oxidative-hydrolytic and tautomeric transformations, possess a high oxidation-reduction potential, and form complexes with metals of variable valency. The most important property of humic acids, which opens the possibility of mobilizing undigested forms of phosphorus, is their acidity. The acidic properties of these natural compounds are due to the presence of carboxyl and phenol groups in their structure.

The role of humic acids in agriculture is extremely important. More precisely, not the acids themselves, as they are insoluble in water and do not exist in physiologically active forms, but their sodium, potassium, and ammonium compounds, which are highly effective growth stimulants for plants. Low concentrations of humates in the solution of 0.0001-0.0500% are effective, and higher concentrations suppress the plant's vital activity. Optimal concentrations depend on the humic acid composition and soil-climatic conditions. This not only increases yields but also accelerates ripening times and improves product quality.

The biological activity of humic acids is determined by their ability to form soluble humates with alkalis, i.e., the content of carboxyl groups and phenolic hydroxyls; their

ability to participate in oxidation-reduction reactions in the plant cell, i.e., the content of chinoid groups and phenolic hydroxyls; the content of free radicals, and other factors.

The physiologically active substances of soil humus and fertilizers influence the overall course of plant metabolism by enhancing oxygen absorption, activating enzymes (primarily respiratory cycles), enhancing chlorophyll formation, changing the forms of phosphorus compounds, and increasing mono- and disaccharide and protein content in the harvest. Thanks to humus substances, a diverse microbial population is maintained in the soil. The application of carbon-humic fertilizers significantly increases the biochemical activity of agronomically valuable groups of microorganisms. The agronomic role of humic substances is manifested in the improvement of soil structure, aeration, water retention, and water permeability. In light soils, this phenomenon is observed in aggregation processes, while in heavy soils, it is observed in obstacles to the formation of crusts and cracks. However, the most important factor is increasing the availability of phosphorus through chelation, which prevents its fixation by iron and aluminum, and in carbonate soils, its retrogradation. Plants use the phosphorus of superphosphate mixed with manure better than when both fertilizers are applied separately to the same soil. Due to the chelating properties of organic matter, phosphates are formed in forms accessible to plants. Industrial combination of phosphorus with humic molecules allows obtaining new forms of fertilizers with increased phosphorus use[9].

Results. In recent years, advanced agricultural technologies have been developed and introduced. To consider issues related to the hardware and technological design of individual stages of specific processes, data justifying the selection of their implementation parameters is necessary. This is achieved through the rational apparatus design of the process and the regulation of its temperature-concentration conditions.

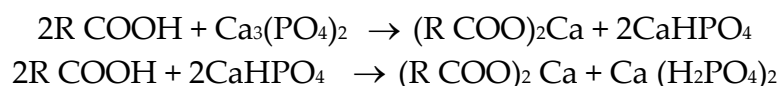
To conduct the experiments, ground phosphate raw materials, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sulfur, urea, and leonardite (total humus content 52.3-64.5%; organic matter 66.7-71.1%; moisture content 26.53-33.07%) were used as starting materials.

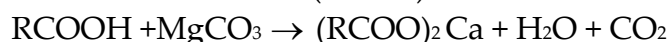
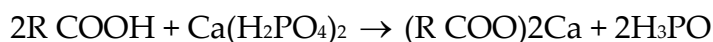
The research was conducted in a glass reactor equipped with a vane stirrer and placed in a thermostated container.

In a thermostated beaker, ground phosphate raw materials, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sulfur, urea, and leonardite (total humus content 52.3-64.5%) were placed and mixed with water, then the resulting suspension was intensively stirred for 10 minutes at 70-80°C.

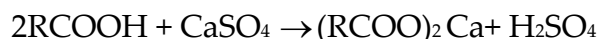
Further, the pulp was dried to constant weight at 100-105°C. In this case, a product is obtained (in mass. P_2O_5 total. = 17.9; P_2O_5 sol. = 6.37; P_2O_5 p.s. = 6.01; Nover. = 1; CaO total = 34.0; CaO p = 10.0; MgO = 1.4; SO total. = 11.35; SO_3 p.p. = 2.0; Total organic matter = 8.0; PH=7.28 and others.

The reactions between humic acids and phosphates can be depicted as follows[10,11]:

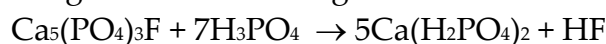
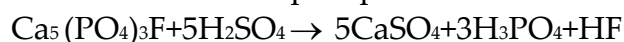




The reactions between humic acids and natural gypsum can be depicted as follows[12]:



Then the formed H_2SO_4 reacts with phosphates:



In the humus-accumulative horizons, sulfur accumulates mainly in the form of organic compounds. They contain the main part of the soil sulfur. As a result of microbiological processes, it oxidizes to sulfates, which are then absorbed by plants and can accumulate by them up to 0.02-1.8%. However, the use of sulfate-containing fertilizers is not without its drawbacks, including the acidification of the soil solution and the high rate of sulfate ion migration along the soil profile in soils with a flushing water regime. Despite the apparent effectiveness of using elemental sulfur as a fertilizer, it has not been widely adopted in agriculture. It is more known as a contact fungicide with protective action against a number of plant diseases[13].

Discussion. The application of humic simple superphosphate in agriculture will undoubtedly increase the humus content in the soil, significantly improving its structure and physical-mechanical properties. By containing all the necessary nutrients for plants, the possibility of obtaining higher and better yields is created, increasing the nutritional properties of plants and their resistance to diseases. When applying humic fertilizers, first of all, the physical properties of the soil change, the capillary and field moisture capacity of light soils and the water permeability of heavy soils increase, the structure and its water resistance improve, the soil density decreases, and the conditions for soil nutrition of plants change significantly, namely: the mobility of soil phosphorus increases; nitrate formation processes intensify in the soil, which contributes to a significant increase in total and protein nitrogen and the predominance of nitrates over ammonia nitrogen, and the increase in the release of carbon dioxide by the soil. Nitrogen fixation and the availability of organic nitrogen in the soil for plants also increase; the intake of ammoniacal and amide forms of nitrogen and phosphorus into plants accelerates.

The total sales volume of humic preparations and fertilizers in various countries has increased hundreds of times over the past decade. Agrotechnical methods for applying them to the soil, including in conjunction with mineral fertilizers, have been introduced into the practice of several advanced agricultural countries: the USA, Canada, Spain, and Italy. Recently, the Chinese market for humates, as well as a number of large companies producing mineral fertilizers, has been growing rapidly.

The use of such fertilizers allows increasing the yield of agricultural crops and the quality of the agricultural products obtained, ensuring the restoration of soil humus and

maintaining soil fertility. The price of such fertilizers is significantly higher, which is one of the main factors hindering the rapid expansion of the market. However, according to reputable experts, good prospects open up for producers of these types of fertilizers[14].

Conclusion. Thus, humic acids are important components of the natural system, ensuring the maintenance of soil fertility and in agriculture, reducing the need for nitrogen fertilizers, increasing the utilization rate of phosphorus fertilizers, and reducing food and environmental pollution.

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